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Nodulation of electrodeposited copper in the presence of thiourea

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This paper considers the effect of thiourea concentration, temperature and current density on electrodeposited copper nodulation. Thiourea concentration was varied from 0 to 60 mg dm^{-3} in the range 30 to 60° C and at current densities of 21.5, 48.4, 75.3 and 129.2 mA cm^{-2}. Thiourea was found to initiate nodulation and this effect was always associated with a large increase in overpotential, i.e., > 100 mV. This phenomenon occurred only when the applied current density was greater than a critical current density, i_c. The critical current density was found to be insensitive to potential over a range of about 100 mV. Also, it decreased nonlinearly but smoothly with increase in thiourea concentration at a given temperature and increased similarly with temperature at a given thiourea concentration. Galvanostatic experiments were carried out to study this phenomenon and a qualitative explanation is given based on potentiodynamic measurements and suppositions as to the possible chemical reactions taking place at the cathode surface based on evidence in the literature.

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1. Introduction

In the electrolytic production of copper, control of cathode growth while maintaining high current efficiency is very important. This is difficult and complex because cathode growth is affected by many variables such as: (a) quality of the anode, (b) electrolyte composition and impurities, (c) current density, (d) surface conditions of the starter cathode, (e) uniformity of spacing between electrodes and (f) temperature.

With typical current densities in industrial copper electrorefineries at 30 to 40% of the limiting current density mass transfer can not be neglected and in many cases it causes rough copper deposits. As a consequence if the current density is increased sufficiently due to uneven current distribution some of the rough spots produced on the copper surface will grow faster than the substrate in a nodular fashion. These nodules may eventually contact the anode causing short circuits with concomitant problems such as: (a) unacceptable copper cathodes which require reprocessing; (b) current efficiency decreases and hence operating cost increases due to short circuits; and (c) possible lower recovery of byproducts. In a very competitive market, these factors are critical to commercial production of cathodes.

Nodulation prevention is of high priority in successful operation of tankhouses and it is the major concern in overall cathode quality. Nodulation is suppressed by proper selection of temperature, current density, copper and acid concentration in the electrolyte and probably more importantly by proper use of addition agents. In most refineries operating presently, addition agents consist of animal glue, thiourea (TU), chloride ion and in some cases a sulphonated hydrocarbon [1–4]. TU is reported, however, as the addition agent most commonly used.

The reason for nodulation is not clearly known but it is generally considered to be due to an upset in the balance of addition agents. Andersen, *et al.* [5] have shown that nodules can be seeded by minute conducting particles, especially copper, formed in anode slimes and deposited on the cathode. More recently it has been observed that TU by itself [6, 7] and TU in the presence of chloride ion [2, 6, 7, 8] can initiate nodulation. Thus, the very additives used to suppress nodulation if not properly controlled can in fact cause the problem. The balance of addition agents as a function of localized current density and temperature becomes extremely important in nodulation control. In most cases the balance of addition agents is optimized by refineries by a trial and error basis, though some refineries have gone to control based on measurement of the cathode overpotential [9–17].

The inhibiting and depolarizing effects of additives, especially TU, are well documented in the literature [2, 18–42]. Among the characteristics of addition agents their inhibiting effect on the deposition of copper and the influence on the copper morphology (levelling effect) are the more prominent. A characteristic depolarizing effect in some addition agents has also been observed [2, 43–45]. When this phenomenon occurs the cathodic overpotential decreases for a given current density in comparison to overpotentials obtained when no additive is present at the same conditions. Except for the work of Andersen *et al.* [5] Padilla *et al.* [8], O'Keefe [2] and Winand *et al.* [21],

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little has been reported on the effect of addition agents on the phenomenon of nodulation, nodule growth and suppression at different temperatures and current densities.

Thiourea (TU) is oxidized in the presence of cupric ions to produce formamidine disulphide (FDS) as follows [22]:

$$2Cu^{2+} + 2(NH_2)_2CS \rightleftharpoons 2Cu^{+} + (NH_2)_2(NH)_2C_2S_2 + 2H^{+} \qquad E_0 = 0.578\,V \quad (1)$$

TU also forms a redox couple with FDS:

$$2TU \rightleftharpoons FDS + 2H^{+} + 2e^{-} \qquad E_0 = 0.420\,V \quad (2)$$

Both TU and FDS complex with cuprous ion [2]:

$$Cu^{+} + TU \rightleftharpoons [Cu(TU)]^{+} \quad (3)$$

$$Cu^{+} + FDS \rightleftharpoons [Cu(FDS)]^{+} \quad (4)$$

Also TU complexes with cupric ion,

$$Cu^{2+} + TU \rightleftharpoons [Cu(TU)]^{2+} \quad (5)$$

At the low levels of TU used in refineries it is doubtful that free TU ever exists.

Wang and O'Keefe [2] reported a depolarizing effect of TU on the copper deposition at concentrations below 5 p.p.m. At higher concentrations a polarizing effect was observed. These phenomena were explained in terms of cuprous formamidine disulphide $[Cu(FDS)]^{+}$ and the cuprous thiourea $[Cu(TU)]^{+}$ complexes. At low concentrations of TU, $[Cu(FDS)]^{+}$ is considered to be more predominant than $[Cu(TU)]^{+}$. This is in agreement with polarographic work [22], which has shown that the cathodic reduction wave of FDS is present only at high concentrations of TU. This can be explained by assuming that at low TU concentrations FDS exists only as $[Cu(FDS)]^{+}$ and there is no free FDS available to produce the cathodic reduction wave.

The $[Cu(FDS)]^{+}$ formed is apparently reduced to TU and copper relatively easily, allowing the TU produced to react chemically with Cu^{2+} forming more FDS as follows:

$$[Cu(FDS)]^{+} + e^{-} \rightleftharpoons Cu^{0} + FDS \quad (6)$$

$$FDS + 2e^{-} + 2H^{+} \rightleftharpoons 2TU \quad (7)$$

$$2TU + 2Cu^{2+} \rightleftharpoons 2Cu^{+} + FDS + 2H^{+} \quad (8)$$

$$2Cu^{+} + 2FDS \rightleftharpoons 2[Cu(FDS)]^{+} \quad (9)$$

Reactions 6, 7, 8 and 9 are more likely to happen at low overpotentials as well as low concentrations of TU, as will be seen later.

A typical current density against overpotential polarization curve at a relatively high concentration of TU is shown in Fig. 1 [2, 6]. A region of the curve in Fig. 1 can be seen where current density is insensitive to overpotential, this current density is defined as the "critical current density", i_c. The application of a current density higher than i_c during a galvanostatic experiment results in a sudden increase in the overpotential to a value defined here as E_2. The implications of this phenomena on nodulation of copper are not documented.

This paper describes a study of the effect of thiourea on the phenomenon of nodulation at different experimental conditions of current density and also of temperature. Of particular concern will be levels of TU that cause nodulation.

2. Experimental details

Figure 2 shows the three-electrode apparatus used for nodulation studies. A Plexiglass cover served to hold the cathode and the anode. The cathode was 1.7 cm × 1.7 cm, and the substrate consisted of a stainless steel sheet where copper was electrodeposited

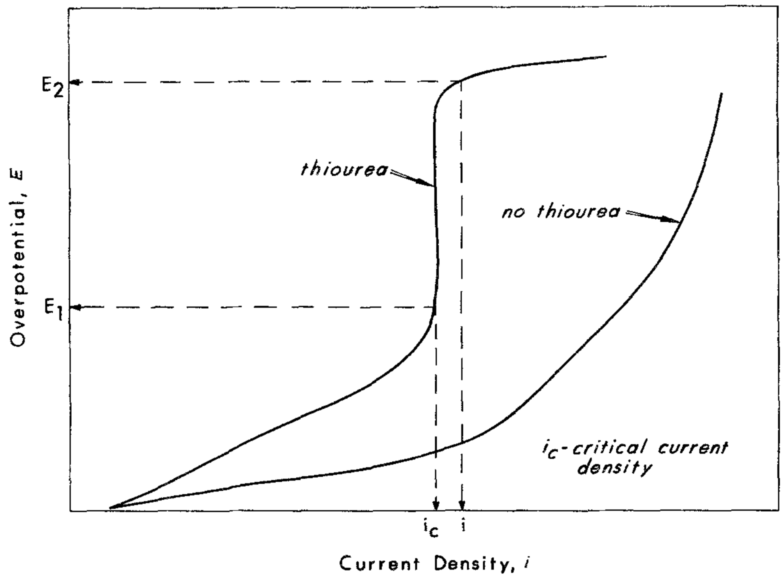

Fig. 1. Polarization curve showing the inhibiting effect of thiourea on the deposition of copper.

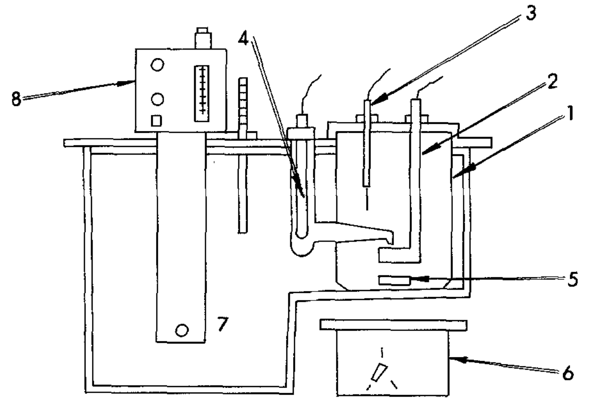

Fig. 2. Schematic drawing of the experimental apparatus. Key: 1. glass cell, 2. stainless steel cathode, 3. platinum anode, 4. reference electrode, 5. magnetic bar, 6. magnetic stirrer, 7. water bath, and 8. Haake constant temperature circulator.

at the beginning of each experiment for 10 to 30 min depending on the current density. This was done at the same copper concentration, temperature and current density as the subsequent nodulation study. Prior to each experiment the cathodes were abraded with 320 grit paper, rinsed with acetone and double distilled water and introduced directly into the experimental cell.

A platinum electrode of approximately 0.48 cm^2 was used as anode. It was kept in a dilute nitric acid solution, rinsed prior to each experiment with double distilled water and introduced into the cell at a distance of approximately 2.5 cm from the cathode. A saturated calomel electrode was used as reference electrode and it was connected to the working electrode (cathode) through a luggin capillary as shown in Fig. 2. The electrolyte consisted of 300 cm^3 of 0.7 M Cu(II) (45 g dm^{-3}) and 1.94 M sulphuric acid (190 g dm^{-3}). No chloride ion was added in this study but was considered in other studies [6–8]. TU was dissolved separately to yield a stock solution which was then refrigerated to minimize deterioration.

The procedure followed was to bring the electrolyte to a required temperature within ± 0.1° C. The copper was preplated and TU solution of desired concentration was then introduced and mixed for 2 min using a magnetic stirrer. The stirrer was then stopped and it was not used thereafter in the experiment. Plating was then initiated for the timed experiment with cathode potential being noted as a function of plating time. After an experiment was completed the cathode was carefully rinsed with distilled water, air dried and the copper coupon was then removed from the cathode for nodule measurements or for scanning electron microscope (SEM) studies.

Potentiodynamic measurements were conducted using the same cell used for nodulation studies, except for the use of a circular copper working electrode having an area of 0.32 cm^2 instead of the stainless steel cathode used previously. The procedure for these experiments and preparation of the electrode was similar to the technique in the nodulation studies except that prior to the introduction of TU copper was plated at a current density of 48.4 mA cm^{-2} for 5 min followed by the recording of a voltammogram without TU. Addition and mixing of the desired TU solutions were then done for the voltammograms. The voltammograms were begun very close to the rest potential and the scan was driven in a cathodic direction to a preset maximum potential at a scan rate of 1 mV s^{-1}, thus they were always forward scans. The voltammograms were obtained with a model 173 Electrochemistry Device having a model 376 Logarithmic Current Converter (Princeton Applied Research).

Copper morphology was determined using the SEM and the optical microscope. Samples from copper coupons were mounted using epoxy resin and a standard SEM technique was followed for sample preparation.

3. Copper morphology

Selected photographs of morphologies and cathode overpotentials obtained in galvanostatic experiments at current densities from 21.5 to 129.2 mA cm^{-2} at temperatures of 30, 40, 50 and 60° C and TU concentrations of 2 to 60 mg dm^{-3} are shown in Figs 3–7. These figures typify results obtained from over a hundred photographs and as portrayed elsewhere [7] for 15 results from which Figs 3–7 have been selected. They show that the appearance of nodules is clearly related to a sudden increase in overpotential. Figure 3 shows that at 40° C with a high current density (129.2 mA cm^{-2}) and at about 2 mg dm^{-3} of TU the overpotential increased and simultaneously nodules appeared. The same correlation is seen between overpotential increase and nodule appearance in Figs 5 and 7. In Fig. 5 it occurred at 50° C and inter-

Table 1. Relationship of temperature and current density to the first appearance of nodulation as a function of thiourea concentration, C_c

i *(mA cm^{-2})*	C_c *(mg dm^{-3})*	*Data sources*
At 30° C		
21.5	~ 10	Fig. 22 [7]
48.4	~ 10	Fig. 23 [7]
75.3	2	Fig. 24 [7]
At 40° C		
21.5	~ 30	Fig. 25 [7]
48.4	~ 30	Fig. 26 [7]
75.3	10	Fig. 27 [7]
129	2	Fig. 3
At 50° C		
21.5	> 60*	Fig. 4
48.4	30	Fig. 30 [7]
75.3	20	Fig. 5
129	10	Fig. 36 [7]
At 60° C		
21.5	> 60*	Fig. 6
48.4	> 60*	Fig. 34 [7]
75.3	30	Fig. 7
129	10	Fig. 36 [7]

C_c = approximate concentration of thiourea (TU) below which there is no nodulation and above which it occurs.
* At these values of C_c no nodulation occurred.

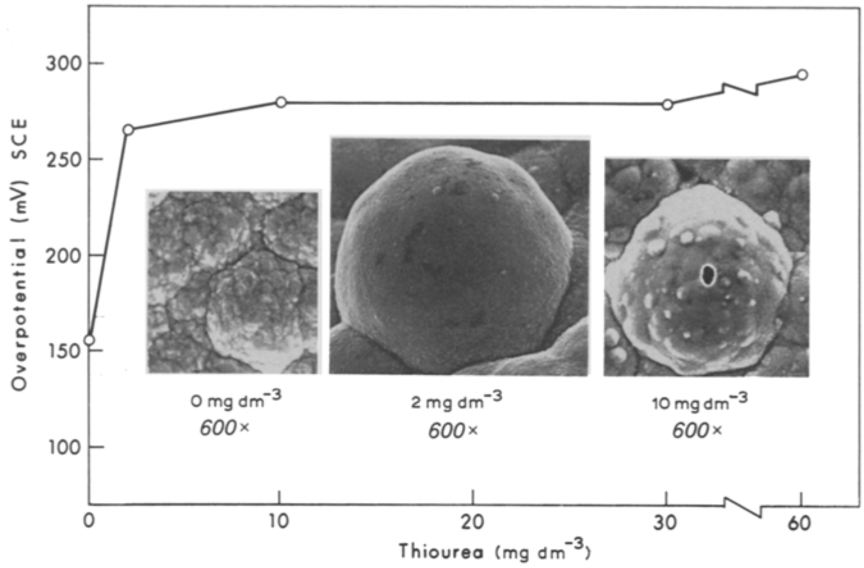

Fig. 3. Effect of thiourea on copper morphology at 40°C and 129.2 mA cm^{-2}.

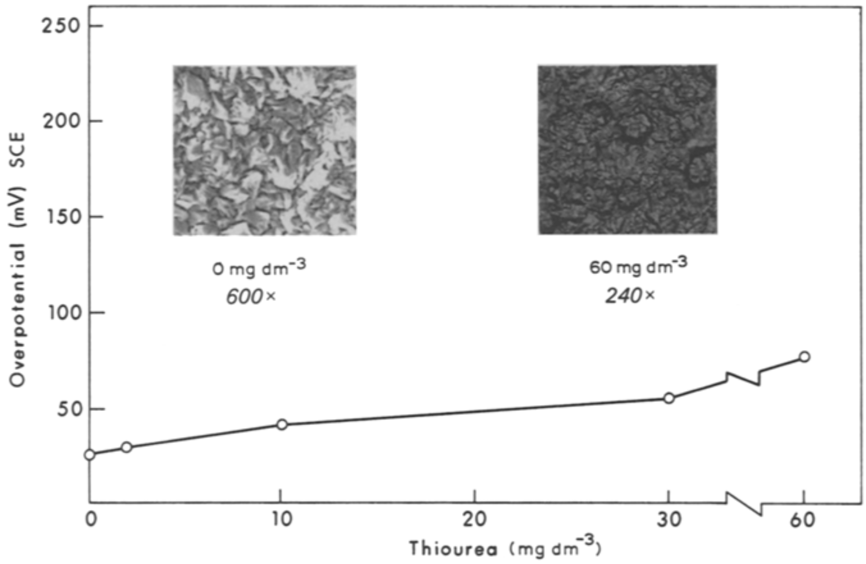

Fig. 4. Effect of thiourea on copper morphology at 50°C and 21.5 mA cm^{-2}.

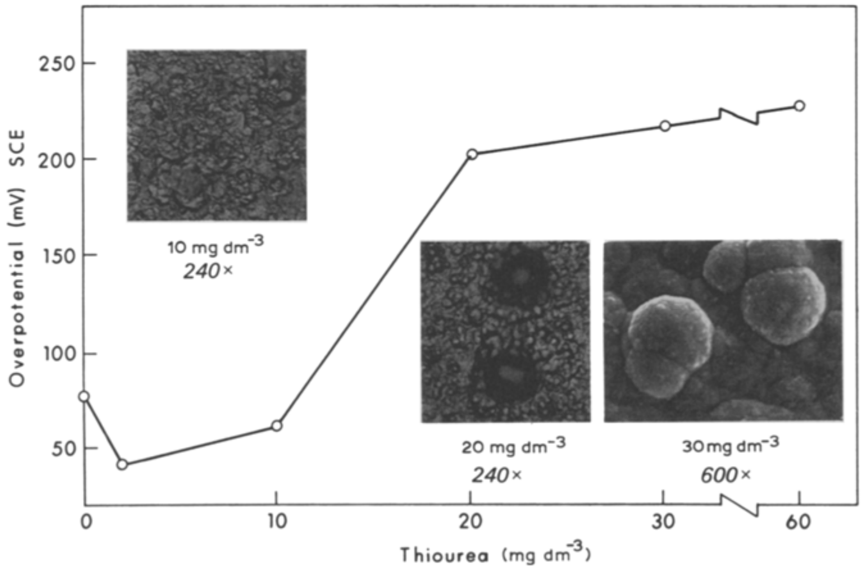

Fig. 5. Effect of thiourea on copper morphology at 50°C and 75.3 mA cm^{-2}.

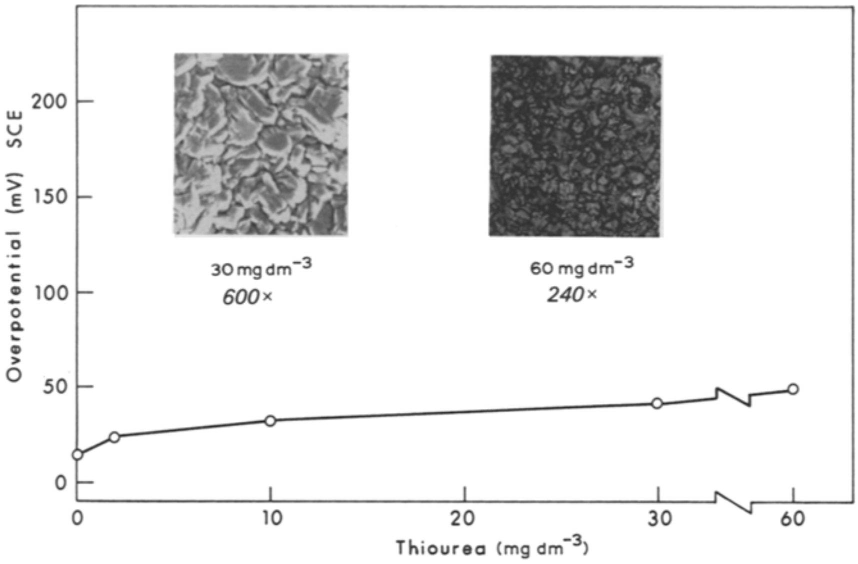

Fig. 6. Effect of thiourea on copper morphology at 60° C and 21.5 mA cm^{-2}.

mediate current density (75.3 mA cm^{-2}) but at about 20 mg dm^{-3} TU and in Fig. 7 at the same intermediate current density but at 60° C, in this instance however with about 30 mg dm^{-3} TU. Figures 4 and 6 show that no increase in overpotential occurred, nor did nodulation appear even at TU levels up to 60 mg dm^{-3}. For Fig. 4 this was at low current density (21.5 mA cm^{-2}) and at 50° C, and for Fig. 6 at this same low current density but at 60° C.

Table 1 summarizes the results of these five figures and also the further results referred to in the previous paragraph [7]. Table 1 uses a term C_c, which is defined as the concentration of thiourea below which there is no nodulation and above which it occurs. These results show that as temperature increases for a given current density C_c increases, i.e., at $i = 75.3$ mA cm^{-2}, $C_c = 2$, 10, 20 and 30 mg dm^{-3} at the respective temperatures 30, 40, 50 and 60° C. Also at a given temperature as i increases C_c decreases. For example at 30° C for respective values of $i = 21.5$, 48.4 and 75.3 mA cm^{-2}, $C_c = \sim 10$, ~ 10 and 2 mg dm^{-3} of TU. The latter correlation from Table 1 is not as clear as the former nor are the other similar correlations from Table 1 but they and other results from Figs 3–7 justify the conclusions: (a) that the level of C_c required for nodulation is directly related to temperature at a given current density and inversely related to current density at a given temperature, and (b) there is a correlation between nodulation, overpotential and C_c. Unfortunately the data are not accurate enough to develop a quantitative relationship for nodulation using the parameters C_c, i, temperature and overpotential.

4. Potentiodynamic measurements

A series of potentiodynamic measurements as a function of TU concentration were made at 30, 40, 50 and 60° C and are reported elsewhere [7]. Only one set, the one measured at 30° C is shown here as seen in Fig. 8. The curves at the higher temperatures are similar in general shape but as temperature increases the critical current density at a given concentration of thiourea also increases. These measurements do not show a well defined Tafel region in the presence of thiourea. It is known that the activity of the cathodic surface

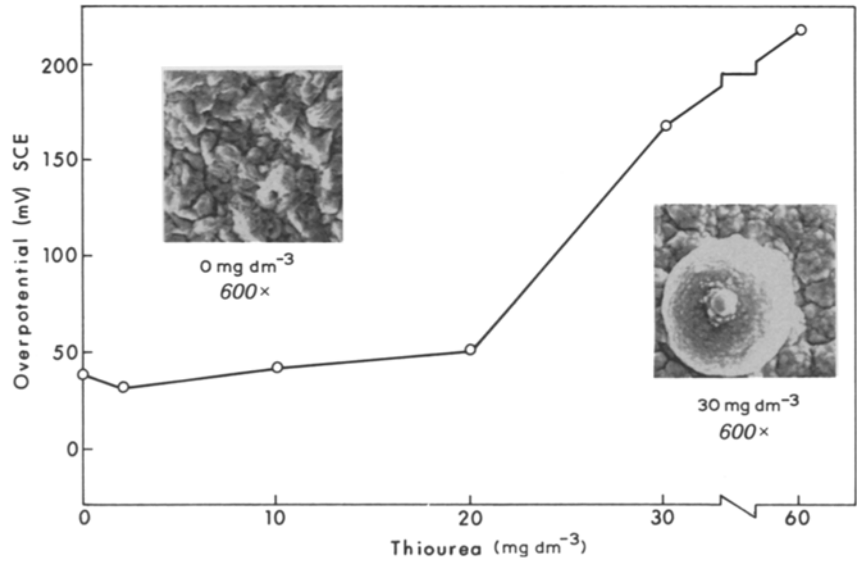

Fig. 7. Effect of thiourea on copper morphology at 60° C and 75.3 mA cm^{-2}.

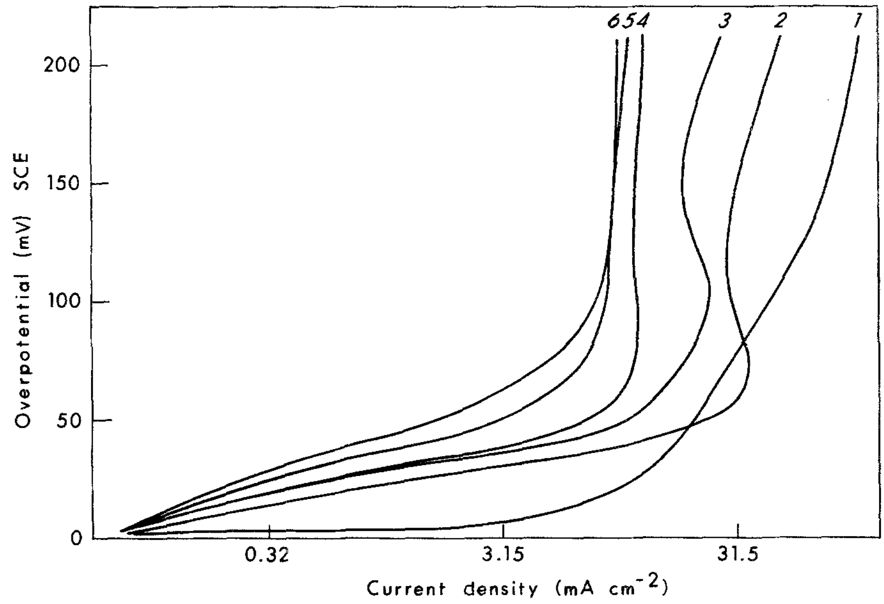

Fig. 8. Potentiodynamic measurements at 30°C and at different concentrations of thiourea. (1) 0, (2) 2, (3) 6, (4) 10, (5) 30, and (6) 60 mg dm^{-3}.

decreases in the presence of additives due to their blocking effect on the surface active sites [33, 34]. This phenomenon along with diffusion of cupric ions through an adsorbed complex may account for the absence of the Tafel region.

4.1. *Thiourea concentration*

Figure 8 shows the following: (a) at low concentration of TU (2 mg dm^{-3}) depolarizing of the cathodic surface occurs between 50 and 80 mV (SCE); (b) again at 2 mg dm^{-3} TU as the cathodic overpotential increases beyond 80 mV, the cathodic deposition becomes inhibited; (c) as TU concentration increases the inhibiting action increases and the depolarizing effect seen at 2 mg dm^{-3} TU disappears; (d) the concentration of TU above which this depolarizing action is not observed is not well defined in Fig. 8 but is less than 6 mg dm^{-3} (curve 3) but greater than 2 mg dm^{-3} (curve 2); and (e) as TU increases to 30 mg dm^{-3} and above, the maximum current density obtained becomes essentially independent of TU concentration. The current density that is independent of potential, i_c (Fig. 1), becomes better defined as TU concentration increases to 10 mg dm^{-3} and above. The expected sudden increase of overpotential (point E_2 in Fig. 1) when the applied current density is higher than i_c is not shown in Fig. 8 because of the nature of the measurement.

The polarizing and depolarizing effects of TU are probably related to the relative concentrations of $Cu(FDS)^+$, $Cu(TU)^{2+}$ and $Cu(TU)^+$ complexes on the surface of the electrode. At low concentrations of TU and low overpotentials the predominance of $Cu(FDS)^+$ over the other complexes is greater and due to the ease with which copper can be plated from this complex (Equation 6) as compared to the other two [2] a depolarizing effect is observed. As the overpotential increases at low TU concentration, or at higher TU concentration in the well defined i_c region, the concentration of TU on the surface increases due to Equation 7 (reverse of Equation 2) and TU tends to produce more $[Cu(Tu)]^+$ (Equation 3) and $[Cu(Tu)]^{2+}$ (Equation 5) than $[Cu(FDS)]^+$ (Equation 4) increasing their relative concentrations with respect to $[Cu(FDS)]^+$. Thus, at high TU concentrations i_c is less. Also, as the TU concentration increases the FDS is more likely to be found uncomplexed [22].

$[Cu(TU)]^+$ and $[Cu(TU)]^{2+}$ reduce by the respective reactions:

$$[Cu(TU)]^+ + e^- \rightleftharpoons Cu^0 + TU \qquad (10)$$

$$[Cu(TU)]^{2+} + 2e^- \rightleftharpoons Cu^0 + TU \qquad (11)$$

Figures 9 and 10 show schematically a mechanistic picture of the depolarizing and polarizing effects of

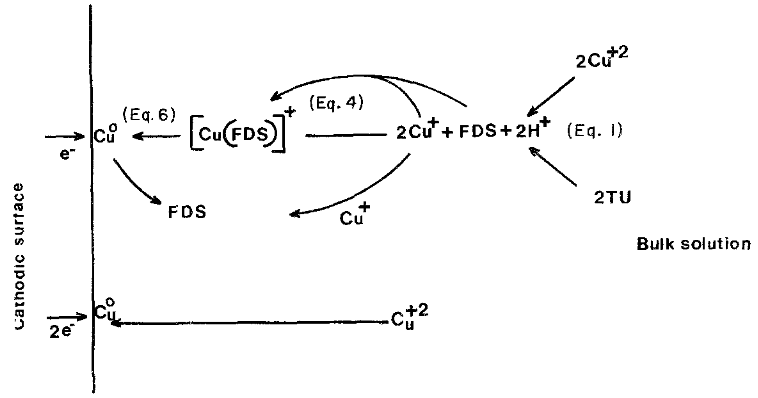

Fig. 9. Mechanistic deposition of copper at relative low concentrations of thiourea and low overpotentials.

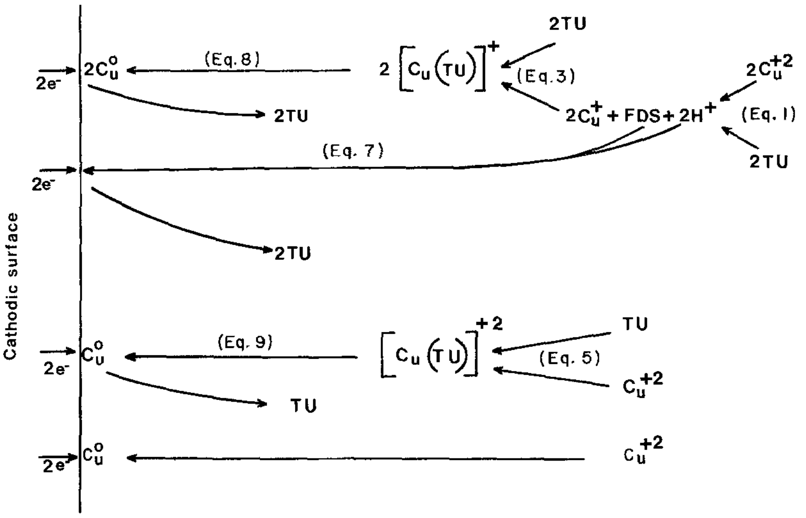

Fig. 10. Mechanistic deposition of copper at relative high concentrations of thiourea and high overpotentials.

TU. Figure 9 corresponds to the deposition of copper at low TU concentration and at low cathodic overpotentials, and Fig. 10 at high concentrations of TU and high cathodic overpotentials.

4.2. *Current density*

Figure 11 shows i_c values which were obtained from Fig. 8 at 200 mV overpotential for various TU levels. Figure 11 also includes i_c values at other than 30° C based on the data reported elsewhere [7]. The 200 mV overpotential portrayed was chosen because at TU $<$ 10 mg dm^{-3} the current density is not truly independent of potential at overpotentials greater than about 50 to 80 mV conditions. It is seen from Fig. 11 that i_c decreases smoothly and non-linearly with increase in initial TU concentration at any given temperature. Also, it is evident that conversely i_c increases with temperature at a given level of TU.

Table 2 is a tabulation of i_c values from Fig. 11 corresponding to C_c values obtained from Table 1 at each current density given there for each temperature. Table 2 also gives values of $i - i_c$, i.e., the difference between the applied and critical current densities. Also shown is whether or not nodulation occurred at each of the given i_c and temperature values. The results are qualitative but show that only when $i - i_c$ is positive, i.e., the applied current density is greater than the critical current density, does nodulation occur. Also utilizing Table 2 it is evident from Figs 3–7 that only for $i > i_c$ is the overpotential large.

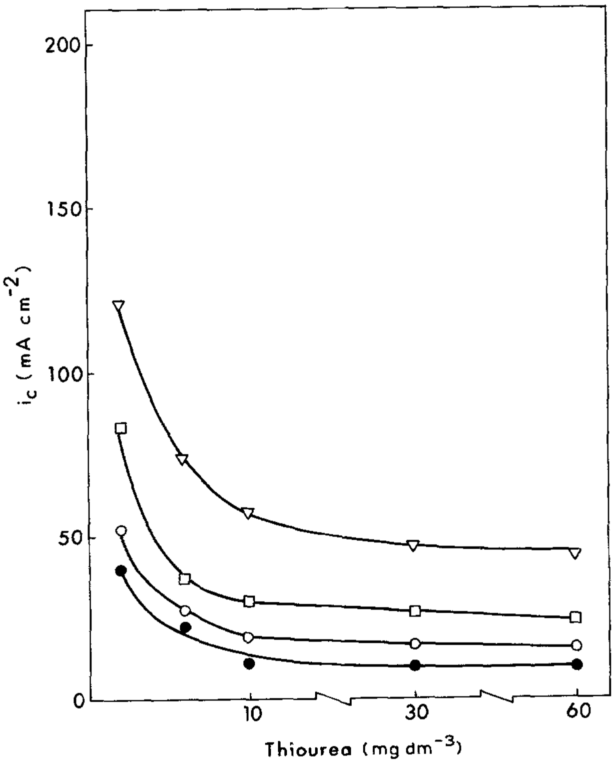

Fig. 11. Critical current densities allowed by the inhibited copper deposition as a function of initial thiourea concentration at 200 mV overpotential (SCE) and at different temperatures. (▽) 60° C, (□) 50° C, (○) 40° C and (●) 30° C.

Table 2. Comparison of the applied current density and critical current density obtained from galvanostatic and potentiodynamic measurements

i (mA cm^{-2})	i_c (mA cm^{-2})	$i - i_c$ (mA cm^{-2})	*Nodular morphology*
At 30° C			
21.5	~15	~6	yes
48.4	15	33	yes
75.3	40	35	yes
At 40° C			
21.5	~10	~12	yes
48.4	10	~38	yes
75.3	14	61	yes
129	57	72	yes
At 50° C			
21.5	25	−4	no
48.4	30	18	yes
75.3	30	45	yes
129	32	97	yes
At 60° C			
21.5	~50	~−28	no
48.4	~50	~−2	no
75.3	50	25	yes
129	60	69	yes

i – Galvanostatic applied current density
i_c – Critical current density obtained from potentiodynamic measurements corresponding to C_c from Table 1.

Nodulation due to thiourea occurs when the current density applied to the cathode is in excess of the current density that the cathode is willing to accept unless driven galvanostatically, i.e., the potential rises to whatever value is needed to break down the passivated surfaces and give reduction reactions at the cathode. It is not clear what the mechanism is by which a breakdown of the passivated film at some sites occurs due to the large impressed overpotential. It may be that there is desorption of inhibiting copper-thiourea complexes at these certain sites to accomodate the required current. These sites on the electrode surface allow copper to deposit at rather high rates as compared to deposition at sites where the inhibiting complexes are still present. As a consequence a nodular copper morphology with several spherical nuclei all over the cathodic surface results. This process will continue as long as the TU concentration is high enough that the applied current density is higher than the critical current density from Fig. 11.

As thiourea concentration at the surface decreases due to depletion reactions to a level of $i < i_c$ the situation changes. A sudden decrease in overpotential occurs and the nodular copper morphology gradually disappears. This aspect was observed in earlier studies but was not explained [6]. As is evident from Fig. 8 if at a given applied current density TU concentration were to decrease a drop in overpotential similar to Fig. 1 (E_2 to E_1) could take place. The conditions for nodulation by TU no longer exist and a general smoothing of the cathode results.

4.3. *Temperature*

The effects of temperature on i_c (Fig. 11) and hence on nodulation are in a general sense the reverse of the dependence on TU concentration. This probably arises largely because increasing temperature reduces the surface concentration of the various TU complexes. The increase in i_c (Fig. 11) with temperature increase at a given level of TU probably involves to some degree all of the following: (a) the kinetics of copper deposition; (b) the diffusion coefficient of cupric ions and addition agents; (c) complexation reactions; and (d) adsorbability of the complexes formed. The role of temperature was not studied sufficiently to differentiate the relative importance of these various temperature effects.

5. Conclusions

Thiourea (TU) can initiate nodulation. Additives in addition to TU are usually used with industrial electrorefining and this aspect has also been studied at this laboratory [6–8], but TU seems to be necessary to cause nodulation unless nodulation is nucleated by anode slimes [5, 8]. In this study TU alone as an additive has caused nodulation.

This study shows that a critical amount of TU, i.e., C_c, is related to the maximum rate that copper can normally deposit with that level of TU; that maximum rate is the critical current density, i_c, (Figs 1 and 11). When in a galvanostatic situation the applied current density is higher than i_c a characteristic sudden increase in overpotential occurs and a nodular copper morphology develops. This should not normally occur in tankhouse operations because current densities should not exceed i_c. There may be regions of the cathode where excessively large current densities occur leading to the conditions which cause nodulation. Upward excursions in additive concentration decrease i_c and localized temperature increases on the other hand due to nearby short circuits increase i_c (Fig. 11). When i is greater than i_c (Fig. 1) and the marked increase in overpotential occurs the surface is in a situation for surface reactions as typified in Fig. 10. The majority of the surface is now covered with the $[Cu(TU)]^+$ and $[Cu(TU)]^{2+}$ complexes instead of the more easily reduced complex $[Cu(FDS)]^+$ (Fig. 9) which is obtained at low overpotentials and low bulk TU levels. However, in the galvanostatic condition copper deposition must occur and breakdowns of the passivated layer at selected sites allow copper deposition there at a much greater rate than that allowed by $[Cu(TU)]^+$ (Equation 8) or $[Cu(TU)]^{2+}$ (Equation 9). Presumably direct reduction of Cu^{2+} or of $[Cu(FDS)]^+$ (Equation 6) occurs. Nodules then develop on the surface. The TU added to give a smooth copper surface which is free from nodules has in fact caused them.

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